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(54) **Plasticizers and processing aids for elastomers**

Weichmacher und Verarbeitungshilfsmittel für Elastomere

Plastifiants et auxiliaires de transformation pour élastomères

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(56) References cited:

US-A- 3 833 689 **US-A- 4 094 927**
US-A- 5 026 807 **US-A- 5 112 725**
US-A- 5 612 418

- **DATABASE WPI Section Ch, Week 8337 Derwent Publications Ltd., London, GB; Class A12, AN 83-763933 XP002106036 & SU 973 565 A (LENGD LENSOFET TECH) , 15 November 1982**
- **DATABASE WPI Section Ch, Week 8642 Derwent Publications Ltd., London, GB; Class A12, AN 86-275190 XP002106127 & JP 61 200135 A (SANYO CHEM IND LTD) , 4 September 1986**
- **DATABASE WPI Section Ch, Week 8148 Derwent Publications Ltd., London, GB; Class A12, AN 81-88529D XP002106037 DU PONT UK LTD: "Polychloroprene compsns. contg. hydroxyalkyl methacrylate derivs. - as reactive plasticisers, enhance flex life without increasing vulcanisate hdnes" A & RESEARCH DISCLOSURE, vol. 211, no. 022, 10 November 1981, Emsworth, GB**

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Description

[0001] The present invention relates to elastomer compositions, a process for preparing the same and methods of plasticizing and/or enhancing processability of elastomers. These compositions have enhanced plasticity and processability with reduced loss of plasticizer from extraction or migration.

[0002] Elastomers are useful in many fields in a variety of applications. For instance, elastomers are used in the automobile, defense, space, oil drilling and oil recovery industries. Elastomers may be fabricated into, for example, tires, seals, gaskets, extruded goods, specialty parts and sheet stock for use in such industries. Consequently, in such applications, parts fabricated from elastomers may have to be resistant to, for example, fuel, lubricants, extreme temperatures, water, steam, or chemicals. Furthermore, depending on the application, such elastomers may be required to be plasticized to provide low temperature flexibility, as well as enhanced elongation and tensile properties. Also, such elastomers are preferred to have a certain amount of processability for efficient and economical fabrication into the required part.

[0003] Plasticizers are added to elastomers to provide or enhance the plasticity of the materials. Specifically, plasticizers are materials which when added to a polymeric material cause an increase in workability and flexibility brought about by a decrease in the glass transition temperature (T_g) of the polymer. Plasticizers are usually of two types, internal and external. Internal plasticizers are made by creating a plasticizing polymer in situ at the same time the polymer is formed. External plasticizers are fully prepared before they are added to the polymer. (*Generally, see Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 19, pages 258-273 for a discussion of plasticizers.*)

[0004] Conventional plasticizers, at times, tend to migrate within the elastomer, "bloom" to the surface and "bleed" from the elastomer so that the effective lifetime of a part fabricated from the elastomer is shortened. This migration is exacerbated by the environments in which some of the elastomeric materials are required to operate. Such environments may cause the plasticizer to be extracted from the elastomer. Subsequently, the plasticization decreases and the environment may be polluted with the plasticizer. One conventional approach in overcoming plasticizer migration problems is by the use of plasticizers having a high molecular weight. However, use of such high molecular weight plasticizers results in elastomer compounding problems. That is, it was very difficult to compound and blend the components into a compatible elastomeric composition. Also, the processability of these elastomers suffer.

[0005] Conventionally, many chemical compositions have been utilized for the purpose of plasticizing polymers to improve the flexibility, low temperature performance, percent elongation before breaking, Shore A hardness, and resistance to tearing and cracking when impacted. Such physical tests are used as an actual indicator of actual performance in a finished product and are well known in the art. For instance, such physical tests are described in *Rubber Technology, second edition, Chapters 4 and 5*.

[0006] Short chain (meth)acrylates have been suggested as plasticizers in rubbers. For instance, hydroxyethyl and hydroxypropyl methacrylates, as well as their alkoxy derivatives, have been suggested as plasticizers in polychloroprene compositions. (*See UK Research Disclosures, Vol. 211, page 403 # 21122*). Also, C₈-C₁₃ alkyl methacrylates, as well as 2-ethoxy-ethyl methacrylates combined with powdered elastomers, i.e., natural rubber, styrene-butadiene, or acrylonitrile-butadiene have been suggested as soft acrylic elastomeric compositions for use in dental prosthesis. Such a combination is said to avoid the use of plasticizers. (*See Parker, S. and Braden, Biomaterials 1990, Vol. 11, September.*) Vulcanized rubber was plasticized with C₇-C₁₂ alkyl methacrylates. (*See Panchenko et al Kauch, I Rezina (4), 24-26 (1979)*). This reference suggests that lower chain methacrylates, i.e., heptyl methacrylate, have the highest plasticizing capacity. In *U.S. patent 5,026,807* a methacrylic acid ester, having a repeating ester group within a long chain alkyl substituent, i.e., between a C₃₋₂₀ alkylene group and a C₁₋₂₀ hydrocarbon group, is used as an elastomer additive. The ester was compounded with a polymer having elasticity to provide a composition having enhanced oil, heat, and low temperature resistance.

[0007] Blends of polyacrylate copolymers and terpolymers of C₄-C₈ alkyl acrylates, C₁-C₃ alkyl acrylates and C₂-C₁₂ alkoxyalkyl acrylates and partially hydrogenated nitrile rubbers are disclosed as useful in automobile engine belts, hoses, gaskets and seals in *U.S. patent 5,612,418*. However, the disclosed compositions also contain a plasticizer additive, which indicates that the polyacrylates were not considered to have plasticizer properties. Possible use of acrylate and methacrylate polymers as plasticizers is suggested in *U.S. patents 4,158,736 and 4,103,093*. However, these patents do not disclose specific elastomer compositions or use in elastomer compositions.

[0008] US Patent No. 3833689 discloses elastomeric compositions comprising olefin-acrylic ester copolymers. US Patent No. 5112725 discloses elastomeric compositions in which an elastomeric binder is compounded with a series of acrylate monomers but additionally requires a polymerisable component having two or more olefinic double bonds. US Patent No. 4094927 discloses a composition comprising a blend of a polyolefin and an alkyl methacrylate. Soviet Union Patent No. 973565 (Lengd Lensovet Tech) discloses mixtures based on butadiene-nitrile rubber comprising oligo-acrylate ester. JP-A-61200135 discloses a plasticizer for rubber consisting mainly of a polycene of molecular weight 400 - 6000 which is obtained by blocking at least one hydroxyl group of a polymer, having a polycene structure as the main chain with terminal hydroxyl group, with a silyl, aryl, allyl or glycidyl group.

[0009] None of these references address the problem of plasticizer migration and plasticizer/elastomer compatibility discussed above. Suitable non-migrating plasticizers which are easily compounded with a variety of elastomers, including elastomers, such as fluoroelastomers which are known to be difficult to compound, have heretofore not been disclosed in the prior art. Accordingly, there is a need for a plasticizer for elastomers which has a substantial amount of permanence within the elastomer composition, but which is also compatible with the elastomer and effectively imparts "plastic" properties to the elastomer. An example of this need may be seen in the compounding of acrylic rubber (ACM) at line 1, paragraph 3 on page 930 of *Kirk-Othmer, Volume 8* where lower concentrations of plasticizers must be used due to plasticizer loss from volatility at the higher typical ACM service temperatures and/or their partial extractability by aggressive fluids where ACMs are employed. Other additives are therefor required to improve processability due to decreased plasticizer levels.

[0010] The present inventors have discovered new elastomer compositions which are plasticized by polymeric materials prepared from at least one ethylenically unsaturated monomer and novel processes for preparing the same. The subject elastomer compositions have enhanced plasticity without attendant migration or compatibility problems associated with prior art elastomer compositions. This is true even in elastomeric materials, such as fluoroelastomers, which have heretofore had no or at best very few plasticizers available for use therein.

[0011] The polymeric compositions of the elastomer compositions of the present invention are present as interpenetrating networks of polymeric plasticizer and/or processing aids within the elastomer polymer matrix. The polymeric (meth)acrylate chains are trapped within the elastomer thereby having an enhanced permanence within the elastomer. This results in increased life to the plasticized elastomer and the ability to add more filler without bleed out of the filling material. This is accomplished without loss of compatibility between the plasticizer and the elastomer.

[0012] In a first aspect of the present invention, there is provided an elastomer composition comprising:

(A) at least one elastomer;

(B) a plasticizer comprising at least one polymeric material, having a weighted average molecular weight of (Mw) of 500 to 1,000,000, formed from at least one ethylenically unsaturated monomer selected from the group consisting of:

(i) at least one monomer selected from the group consisting of (meth)acrylic acid; C₁₀-C₅₀alkyl (meth)acrylates; and C₁-C₅₀alkyl (meth)acrylates substituted with halogen, nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino, alkylamino or dialkylamino; and

(ii) optionally, at least one monomer selected from the group consisting of vinylaromatic monomers, optionally substituted with one or more halogen, nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino, or alkylamino group; nitrogen-containing ring compounds and thio analogs thereof, optionally substituted with C₁-C₈alkyl; vinyl acetate; vinyl chloride; vinyl fluoride; vinyl bromide; vinylidene chloride; vinylidene fluoride; vinylidene bromide; (meth)acrylonitrile; (meth)acrylamide; and dialkylamino-C₂-C₆alkyl (meth)acrylamides, and

(C) a curing agent,

wherein the at least one polymeric material is substantially permanent within the elastomer, such that, during mixing in or with the elastomer, molding or during use of any piece prepared from the elastomer composition, or in response to an external stimulus, the loss of polymeric material from the elastomer is less than 10 percent by weight of the total weight of the at least one polymeric material.

[0013] In a second aspect of the present invention, there is provided a process for preparing an elastomer composition, including: (A) providing a mixture of an elastomer, at least one ethylenically unsaturated monomer as hereinbefore defined or a polymeric material having a weighted average molecular weight of 500 to 1,000,000, formed from at least one ethylenically unsaturated monomer as hereinbefore defined, and a curing agent; and (B) curing the elastomer composition, wherein during curing the at least one ethylenically unsaturated monomer, if present, is polymerized in situ to form an elastomer composition, wherein the at least one polymeric material is substantially permanent within the elastomer, such that, during mixing in or with the elastomer, molding or during use of any piece prepared from the elastomer composition, or in response to an external stimulus, the loss of polymeric material from the elastomer is less than 10 percent by weight of the total weight of the at least one polymeric material.

[0014] In a third aspect of the present invention, there is provided a method of plasticizing an elastomer, comprising: (A) providing an elastomer composition according to the present invention, wherein the at least one polymeric material is present in an amount effective to plasticize the elastomer.

[0015] In a fourth aspect of the present invention, is provided a method of enhancing processability of an elastomer, comprising: (A) providing an elastomer composition according to the present invention, wherein the at least one polymeric material is present in an amount effective to enhance processability of the elastomer.

[0016] As used herein the terminology "(C₁-C₅₀)", "(C₁-C₂₀)" or "(C₂₀-C₅₀)" means a straight chain or branched chain

alkyl group having from 1 to 50, 1 to 20 or 20-50 carbon atoms per group.

[0017] As used herein, the expression "(meth)acrylate(s)" is intended to include both methacrylate(s) and acrylate(s) within its scope.

[0018] As used herein, the term "elastomer" refers to any polymer which undergoes reversible extensibility and includes both elastomers and thermoplastic elastomers. Also, the term "polymeric" is understood to include within its scope all types of molecules characterized as having repeating units of atoms or molecules linked to each other such as oligomers, homopolymers, co-polymers including block, random and alternating co-polymers, grafted polymers and co-polymers, and terpolymers.

[0019] The term "PHR" is understood to mean parts per 100 parts elastomer.

[0020] Throughout this specification and claims, unless otherwise indicated, references to percentages are by weight, all temperatures by degree centigrade and all pressures are atmospheric.

[0021] It is also to be understood that for purposes of this specification and claims that the range and ratio limits, recited herein, are combinable. For example, if ranges of 1-20 and 5-15 are recited for a particular parameter, it is understood that ranges of 1-15 or 5-20 are also contemplated.

[0022] As indicated above, the elastomer compositions of the present invention include at least one elastomer. The elastomer is generally present in the elastomer composition from 20 to 99.9, preferably 40 to 99.9, more preferably 60 to 99.9 percent by weight of the elastomer composition.

[0023] Generally, any suitable elastomer may be used in the elastomer compositions of the present invention. Preferably, the elastomer is a thermosetting, crosslinking elastomer. Suitable elastomers include, but are not limited to, natural rubbers; modified natural rubbers including those grafted with acrylates or those which are halogenated; styrene-butadiene elastomers such as styrene-butadiene rubber (SBR), solution SBR (SSBR), carboxylated SBR (XSBR), high styrene-butadiene copolymer (HS/B), pyridine(vinyl)-styrene-butadiene rubber (PSBR); chloroprene elastomers such as poly-chloroprene elastomers (CR) and carboxylated polychloroprene rubber (XCR); polybutadiene elastomers including 1-2 isomers, hydroxyl, carboxyl, emulsion polybutadiene rubber (EBR), and halogen terminated polybutadiene elastomers; butyl elastomers such as polyisoprene elastomers (IR), isoprene/isobutylene elastomers (IIR), halogenated butyl rubber (HIIR) such as bromobutyl elastomer, chlorobutyl elastomer, and polyisobutylene elastomers; nitrile elastomers such as acrylonitrile-butadiene elastomers (NBR), carboxylated NBR (XNBR), hydrogenated and partially hydrogenated acrylonitrile-butadiene elastomer (HNBR), nitrile-isoprene elastomers (NIR); polyethylene elastomers such as chlorinated polyethylene elastomer and chlorosulfonated-ethylene elastomer; ethylene-propylene elastomers such as co-polymers (EPM) and terpolymers (EPDM) of ethylene and propylene; acrylic based elastomers such as acrylate elastomers (AM), acrylate butadiene elastomer (ABR), and ethylene-acrylic elastomers; silicone elastomers such as organopolysiloxane elastomers; fluoroelastomers; epichlorohydrin elastomer; polyalkenamer elastomers such as elastomers prepared, for instance, from cyclooctene, cyclopentene, or 1,5-cyclooctadiene monomers; organic polysulfide elastomers; urethane elastomers; and mixtures or blends thereof. In one embodiment, the at least one elastomer is a styrene-butadiene elastomer, chloroprene elastomer, butyl elastomer, polybutadiene elastomer, nitrile elastomer, polyethylene elastomer, ethylene-propylene elastomer, acrylic elastomer, silicone elastomer, fluoroelastomer, epichlorohydrin elastomer, polyalkenamer elastomer, polysulfide elastomer, urethane elastomer, mixtures thereof or blends thereof. In a preferred embodiment, the at least one elastomer is an acrylonitrile-butadiene elastomer, hydrogenated acrylonitrile-butadiene elastomer, partially hydrogenated acrylonitrile-butadiene elastomer, modified polyethylene elastomers such as chlorinated or chlorosulfonated polyethylene elastomer, ethylene-acrylic elastomer, styrene-butadiene elastomer, fluoroelastomer, or mixtures or blends thereof. In a more preferred embodiment, the at least one elastomer is acrylonitrile-butadiene elastomer, hydrogenated acrylonitrile-butadiene elastomer, partially hydrogenated acrylonitrile-butadiene elastomer, fluoroelastomer, mixtures thereof or blends thereof. In a most preferred embodiment, the at least one elastomer is a fluoroelastomer.

[0024] The elastomer may also be a thermoplastic-elastomer (TPE) having an elastomeric component and a thermoplastic component. Suitable examples include, but are not limited to polyolefin thermoplastic elastomers, polyester/polyether thermoplastic elastomers, thermoplastic elastomers based on isoprene homopolymers and co-polymers, and urethane thermoplastic elastomers.

[0025] The elastomer compositions of the present invention also include at least one polymeric material formed from at least one ethylenically unsaturated monomer as hereinbefore defined. The polymeric material is generally present in the elastomer composition from 1 to 100, preferably 1 to 50, more preferably 2 to 30 PHR. Generally, the at least one polymeric material present in the elastomer has a weighted average molecular weight (Mw) of 500 to 1,000,000, preferably 500 to 500,000, more preferably 500 to 100,000, most preferably 500 to 50,000.

[0026] Examples of the alkyl methacrylate or alkyl acrylate where the alkyl group contains from 1 to 6 carbon atoms (also called the "low-cut" alkyl methacrylate or alkyl acrylate), are methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl and ethyl acrylate, propyl methacrylate, butyl methacrylate (BMA) and acrylate (BA), isobutyl methacrylate (IBMA), hexyl and cyclohexyl methacrylate, cyclohexyl acrylate and combinations thereof.

[0027] Examples of the alkyl methacrylate or alkyl acrylate where the alkyl group contains from 7 to 15 carbon atoms

(also called the "mid-cut" alkyl methacrylates or alkyl acrylates), are 2-ethylhexyl acrylate (EHA), 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, isodecyl methacrylate (IDMA, based on branched (C₁₀) alkyl isomer mixture), undecyl methacrylate, dodecyl methacrylate (also known as lauryl methacrylate), tridecyl methacrylate, tetradecyl methacrylate (also known as myristyl methacrylate), pentadecyl methacrylate and combinations thereof. Also useful are: dodecyl-pentadecyl methacrylate (DPMA), a mixture of linear and branched isomers of dodecyl, tridecyl, tetradecyl and pentadecyl methacrylates; and lauryl-myristyl methacrylate (LMA), a mixture of dodecyl and tetradecyl methacrylates.

[0028] Examples of the alkyl methacrylate or alkyl acrylate where the alkyl group contains from 16 to 24 carbon atoms (also called the "high-cut" alkyl methacrylates or alkyl acrylates), are hexadecyl methacrylate, heptadecyl methacrylate, octadecyl methacrylate, nonadecyl methacrylate, cosyl methacrylate, eicosyl methacrylate and combinations thereof. Also useful are: cetyl-eicosyl methacrylate (CEMA), a mixture of hexadecyl, octadecyl, cosyl and eicosyl methacrylate; and cetyl-stearyl methacrylate (SMA), a mixture of hexadecyl and octadecyl methacrylate. Mixtures of one or more of low-cut, mid-cut or high-cut (meth)acrylates may also be used.

[0029] In one embodiment, the at least one monomer is a C₁₀ to C₂₀ alkyl (meth)acrylate monomer and the at least one polymeric material is a homopolymer or co-polymer of at least one C₁₀ to C₂₀ alkyl (meth)acrylate monomers. In a preferred embodiment, the at least one monomer is lauryl methacrylate, stearyl methacrylate, isomers thereof or a mixture thereof and the at least one polymeric material is a homopolymer of lauryl methacrylate monomer or stearyl methacrylate monomer or a co-polymer of lauryl and stearyl methacrylate monomers.

[0030] In one embodiment, the at least one monomer is a mixture of the C₁₀ to C₂₀ alkyl (meth)acrylate monomers described above. For instance, such mixtures include, but are not limited to, mixtures of C₁₂-C₁₄ monomers, or mixtures of C₁₈-C₂₀ monomers. In another embodiment, the monomer is a (meth)acrylate and the polymeric material is a terminally unsaturated (meth)acrylate oligomer. In one embodiment, the terminally unsaturated (meth)acrylate oligomer has at least 30 percent, preferably at least 50 percent, and more preferably at least 60 percent terminal unsaturation in the oligomeric chain. In another embodiment, the terminally unsaturated butyl acrylate oligomer has 30 percent to 100 percent, preferably 50 percent to 90 percent, more preferably 60 percent to 80 percent terminal unsaturation in the oligomeric chain. In a preferred embodiment, the monomer is butyl acrylate and the polymeric material is a terminally unsaturated butyl acrylate oligomer.

[0031] The mid-cut and high-cut alkyl methacrylate and alkyl acrylate monomers described above are generally prepared by standard esterification procedures using technical grades of long chain aliphatic alcohols, and these commercially available alcohols are mixtures of alcohols of varying chain lengths containing between 10 and 15 or 16 and 20 carbon atoms in the alkyl group. Examples of these alcohols are the various Ziegler catalyzed Alfol alcohols from Vista Chemical company, i.e. Alfol 1618 and Alfol 1620, Ziegler catalyzed various Neodol alcohols from Shell Chemical Company, i.e. Neodol 25L, and naturally derived alcohols such as Procter & Gamble's TA-1618 and CO-1270. Consequently, for the purposes of this invention, the term alkyl (meth)acrylate is intended to include not only the individual alkyl (meth)acrylate product named, but also to include mixtures of the alkyl (meth)acrylates with a predominant amount of the particular alkyl (meth)acrylate named.

[0032] Another class of suitable ethylenically unsaturated monomers is vinylaromatic monomers which includes, among others, styrene, α -methylstyrene, vinyltoluene, p-methylstyrene, ethylvinylbenzene, vinylnaphthalene and vinylxylenes. The vinylaromatic monomers can also include their corresponding substituted counterparts, such as halogenated derivatives, i.e., containing one or more halogen groups, such as fluorine, chlorine or bromine; and nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino and alkylamino derivatives.

[0033] Another class of suitable ethylenically unsaturated monomers is nitrogen-containing ring compounds and their thio analogs, such as vinylpyridines such as 2-vinylpyridine or 4-vinylpyridine, and lower alkyl (C₁-C₈) substituted C-vinyl pyridines such as: 2-methyl-5-vinyl-pyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinyl-pyridine, 2-methyl-3-ethyl-5-vinylpyridine; methyl-substituted quinolines and isoquinolines, N-vinylcaprolactam, N-vinylbutyrolactam, N-vinylpyrrolidone, vinyl imidazole, N-vinyl carbazole, N-vinyl-succinimide, acrylonitrile, o-, m-, or p-aminostyrene, maleimide, N-vinyl-oxazolidone, N,N-dimethyl aminoethyl-vinyl-ether, ethyl-2-cyano acrylate, vinyl acetonitrile, N-vinylphthalimide. Also included are N-vinyl-thio-pyrrolidone, 3-methyl-1-vinyl-pyrrolidone, 4-methyl-1-vinyl-pyrrolidone, 5-methyl-1-vinyl-pyrrolidone, 3-ethyl-1-vinyl-pyrrolidone, 3-butyl-1-vinyl-pyrrolidone, 3,3-dimethyl-1-vinyl-pyrrolidone, 4,5-dimethyl-1-vinyl-pyrrolidone, 5,5-dimethyl-1-vinyl-pyrrolidone, 3,3,5-trimethyl-1-vinyl-pyrrolidone, 4-ethyl-1-vinyl-pyrrolidone, 5-methyl-5-ethyl-1-vinyl-pyrrolidone, 3,4,5-trimethyl-1-vinyl-pyrrolidone, and other lower alkyl substituted N-vinyl-pyrrolidones.

[0034] Another class of suitable ethylenically unsaturated monomers is substituted ethylene monomers, such as vinyl acetate, vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, vinylidene fluoride, vinylidene bromide, acrylonitrile, methacrylonitrile, acrylic acid and corresponding amides and esters, methacrylic acid and corresponding amides and esters.

[0035] Another class of acrylic and methacrylic acid derivatives is represented by substituted alkyl acrylate and methacrylate and substituted acrylamide and methacrylamide monomers. Examples include (meth)acrylates wherein the

alkyl group is substituted with halogen, such as fluorine, chlorine or bromine; and nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino, alkylamino derivatives and the like.

[0036] Each of the substituted monomers can be a single monomer or a mixture having different numbers of carbon atoms in the alkyl portion. In one embodiment, the monomers are selected from the group consisting of dialkylamino (C₂-C₆)-alkylmethacrylates, dialkylamino(C₂-C₆)-alkyl acrylates, dialkylamino(C₂-C₆)-alkyl methacrylamides and dialkylamino(C₂-C₆)-alkyl acrylamides. The alkyl portion of each monomer can be linear or branched.

[0037] Additional examples of substituted (meth)acrylate monomers are those alkyl methacrylate and acrylate monomers with a dialkylamino group in the alkyl radical, such as dimethylaminoethyl methacrylate and dimethylaminoethyl acrylate.

[0038] Other examples of substituted (meth)acrylate monomer are nitrogen-containing ring compounds (previously described) and dialkylaminoalkyl methacrylamide and acrylamide monomers, such as N,N-dimethylaminoethyl methacrylamide, N,N-dimethyl-aminopropyl methacrylamide, N,N-dimethylaminobutyl methacrylamide, N,N-diethylaminoethyl methacrylamide, N,N-diethylaminopropyl methacrylamide, N,N-diethylaminobutyl methacrylamide, N-(1,1-dimethyl-3-oxobutyl) acrylamide, N-(1,3-diphenyl-1-ethyl-3-oxobutyl) acrylamide, N-(1-methyl-1-phenyl-3-oxobutyl) methacrylamide, and 2-hydroxyethyl acrylamide, N-methacrylamide of aminoethyl ethylene urea, N-methacryloxy ethyl morpholine and N-maleimide of dimethylaminopropylamine.

[0039] Another group of ethylenically unsaturated monomers are C₂₀ to C₅₀ (meth)acrylates formed from C₂₀ to C₅₀ synthetic alcohols. Generally, the (meth)acrylates are formed by reacting a C₂₀ to C₅₀ synthetic alcohols or ethoxylate thereof with a low-cut alkyl (meth)acrylate in the presence of a zirconium catalyst and suitable inhibitor. Suitable alcohols or ethoxylates are available from Baker Petrolite, Inc. St. Louis, Missouri as Unilin™ or Unithox™ products. In one embodiment, the at least one monomer is a (meth)acrylate monomer product prepared from a C₂₀ to C₅₀ alcohol or ethoxylate. Suitable examples of such monomers and preparation of the same are disclosed and described in U.S. Patent No. 5,856,611 issued January 5, 1999.

[0040] The elastomer compositions of the present invention also include a curing agent. The curing agent is generally present from 0.1 to 30, preferably from 0.5 to 20, more preferably from 1 to 20 PHR.

[0041] Suitable examples include sulfur such as powdery, colloidal, precipitated, insoluble and dispersible sulfurs; sulfur containing organic compounds capable of releasing active sulfur with thermal dissociation such as tetramethylthiuram disulfide and 4,4'-dithiomorpholine; organic peroxides such as 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 1,3-bis(t-butylperoxy)isopropylbenzene, dicumyl peroxide, dibutyl peroxide, 1,1-di-t-butylperoxy-3,3,5-trimethylcyclohexane, t-butylcumyl peroxide, t-butylperoxy-isopropyl carbonate; metal oxides such as zinc oxide, magnesium oxide, and lead oxide; quinone dioximes such as p-quinone dioxime and p,p'-dibenzoylquinone oxime; modified alkyl phenolic resins; polyisocyanates; polyamines such as triethyleneteramine, methylenedianiline and diethylenetriamine; metal soaps including sodium stearate and potassium stearate; carboxylic acids and ammonium salts of carboxylic acids such as adipic acid, octadecyldicarboxylic acid, ammonium stearate and ammonium adipate; acid anhydrides such as maleic anhydride, pyromellitic anhydride, and dodecenylsuccinic anhydride; dithiocarbamic acids such as hexamethylenediamine carbamate and zinc dimethyldithiocarbamate; polyepoxides such as 1,6-hexanediol diglycidyl ether and ethylene glycol diglycidyl ether; and polyols such as 1,4-butanediol and 1,1,1-trimethylolpropane.

[0042] As is understood by those skilled in the art, the preferred curing agent will depend on the type of elastomer compositions used. For instance, if the elastomer is natural rubber, styrene-butadiene elastomer, butadiene elastomer, or nitrile elastomer the curing agent is generally sulfur, an organic sulfur containing compound or an organic peroxide. If the elastomer is butyl rubber the curing agent is generally sulfur or quinone diamine. When the elastomer is urethane rubber the curing agent is generally a polyisocyanate, polyamine or organic peroxide. When the elastomer is ethylene-propylene copolymer the curing agent is generally sulfur or an organic peroxide. When the elastomer is a fluoroelastomer the curing agent is an organic peroxide.

[0043] The elastomer compositions of the present invention may also include a crosslinking accelerator to be used in combination with the curing agent. The accelerator provides shortening of cross-linking time, lowering of cross-linking temperature, and improvement in the properties of the crosslinked product. The crosslinking accelerator is generally present from 0.1 to 30, preferably from 0.5 to 20, more preferably from 1 to 10 PHR.

[0044] Suitable examples of crosslinking accelerators include, but are not limited to, mecaptobenzothiazole, tetramethylthiuram disulfide, zinc dimethyl dithiocarbamate, for use with a sulfur curing agent; and 1,3-butanediol dimethacrylate, ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, polyethylene glycol dimethacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, 2,2'-bis(4-methacryloyldiethoxyphenyl)propane, trimethylolpropane trimethacrylate, trimethylolpropane triacrylate, pentaerythritol trimethacrylate, divinylbenzene, N,N'-methylene (bis)acrylamide, p-quinone dioxime, p,p'-dibenzoylquinone dioxime, triazinedithiol, triallyl cyanurate, triallyl isocyanurate (TAIC), bismaleimide for use with organic peroxide curing agents.

[0045] The elastomer compositions of the present invention may also include a filler. The filler is generally present from 5 to 500, preferably from 7.5 to 250, more preferably from 10 to 80 PHR.

[0046] Suitable examples of fillers include calcium carbonate; kaolin clay; natural silica such as crystalline silica, microcrystalline silica, and diatomaceous silica; synthetic silica such as fumed silica, precipitated silica, and silica gel; talc (hydrated magnesium silicate); mica (hydrous potassium aluminum silicate); wollastonite (calcium metasilicate); carbon black or fiber; and glass fiber or spheres.

[0047] Other additives commonly utilized in the art may also be incorporated into the elastomer compositions of the present invention. Such additional additives include, but are not limited to, dispersing agents, softening agents, antioxidants, pigments, flame retardants, scorch retarders, foaming agents, tackifiers, blowing agents, lubricants, UV-stabilizers, impact modifiers, and the like. Such polymer additives are described for instance in *Plastics Additives and Modifiers Handbook*, Edenbaum, Jesse, Editor, Van Nostrand Reinhold, New York, 1992.

[0048] As recited above, a process for preparing an elastomer composition, includes as a first step providing a mixture of an elastomer, at least one ethylenically unsaturated monomer as hereinbefore defined or at least one polymeric material, having a weighted average molecular weight (Mw) of 500 to 1,000,000, formed from at least one ethylenically unsaturated monomer as hereinbefore defined, and a curing agent. The elastomer, the at least one ethylenically unsaturated monomer, the at least one polymeric material and the curing agent are as described above.

[0049] Generally, the mixture is provided by means commonly known in the art. For instance, the mixture may be prepared by combining the constituents using a Banbury mixer, open roll mill, cold lab mill, internal mixer, extrusion mixer, twin roll, or the like. The at least one monomer or at least one polymeric material formed from the at least one monomer is generally added at from 1 to 100, preferably 1 to 50, more preferably 2 to 30 PHR. The curing agent is generally added from 0.1 to 30, preferably from 0.5 to 20, more preferably from 1 to 20 PHR. If used, the additional additives recited above may be added in this step. The amounts of additives used are commonly known in the art.

[0050] Once the elastomer mixture is compounded, the composition is cured using methods known in the elastomer art. The curing conditions will vary depending on the elastomer and curing system used and is generally performed according to elastomer manufacturer specifications. However, the curing is generally effected by heating the elastomer composition at a temperature from ambient temperature to 250°C. The actual curing temperature will be dependent on the elastomer composition prepared and on the curing system utilized. During the curing step the elastomer is cured and the monomer if present is polymerized in situ.

[0051] Once the elastomer is cured and the monomer is polymerized (if required) the cured elastomer composition may be heat aged or post-cured by subjecting the cured elastomer to heat treatment in, for instance, a forced air oven. As with curing, the heat aging or post-curing temperature will be dependent on the type of elastomer composition used.

[0052] The elastomeric compositions of the present invention permits wider use of elastomers in applications of demanding conditions wherein the elastomer is exposed to heat, cold, chemicals, lubricants and the like without migration of the polymeric plasticizer of the present invention. Furthermore, the elastomers would permit a higher level of carbon black or other reinforcing agent or filler into the elastomer thereby improving the properties of the elastomers and/or reducing costs. These properties make them especially useful in down hole oil drilling and recovery operations, as seals, tubing or hoses in engines and in other applications involving corrosive fluid transfer. As a result, of the chemistry of the elastomeric compositions and of the vast range of compounds available for use as plasticizers it is possible to tailor the plasticizer to the elastomer to maintain compatibility while plasticizing and enhancing processability of the elastomer.

[0053] Accordingly, in the elastomer compositions of the present invention the at least one polymeric material is substantially permanent within the elastomer. For the purposes of this specification, including the attached claims, the term substantially permanent means that there will be a minimal amount of loss of the at least one polymeric material plasticizer from the elastomeric composition because of compatibility problems (see below) or in response to an external stimulus such as heat and/or solvent extraction. Generally, the loss of polymeric material (plasticizer) from the elastomer will be less than 10 percent, preferably less than 5 percent, more preferably less than 3 percent, and most preferably less than 1 percent by weight of the total weight of the at least one polymeric material plasticizer.

[0054] By compatibility of the at least one polymeric material and the elastomer is meant that the at least one polymeric material plasticizer remains within the elastomer, i.e., maintains its position within the elastomer during mixing (also is able to be mixed into the elastomer), molding and during use of any piece prepared from the elastomer composition. The plasticizers of the present invention do not change positions or migrate ("bloom") to the surface of the elastomer composition.

[0055] As recited above, a method of plasticizing an elastomer is also contemplated. The method includes providing an elastomer composition according to the present invention, wherein the at least one polymeric material is present in an amount effective to plasticize the elastomer. Generally the at least one polymeric material is present from 2 to 100, preferably from 2 to 60, more preferably from 2 to 30 PHR.

[0056] Also contemplated, is a method of enhancing processability of an elastomer, including: providing an elastomer composition according to the present invention, wherein the at least one polymeric material is present in an amount effective to enhance processability of the elastomer. Generally, the at least one polymeric material is present from 2 to 30, preferably from 2 to 20, more preferably from 2 to 10 PHR.

[0057] The following Examples are provided as an illustration of the present invention.

EXAMPLE 1

Preparation of Nitrile Rubber Elastomer Composition

[0058] An elastomer mixture containing:

	PHR
Chemigum N615B (nitrile rubber from Goodyear-Akron, Ohio)	100
Akro-Zin Bar 85 (85% Zinc disp from Akrochem- Akron, Ohio)	5
Flectol Pastilles (processing aid from Harwick-Akron, Ohio)	3
N 774 carbon Black (from Cabot - Norcross Georgia)	60
WB 2222 (Anti-oxidant from Structol - Stow, Ohio)	1
Peroximon DCP40 (40% Dicumyl peroxide from Akrochem-Akron, Ohio)	6

was compounded by combining the materials, on a cold lab mill for ten (10) minutes while not exceeding a temperature of 50 deg C. No plasticizer was included in the elastomer composition. The green elastomer composition was cured into 2.54mm (100 mil) test sheets at 160 deg C for 25 minutes. The cured elastomer material was measured for Tg by DMTA, Shore A Hardness (ASTM D2240), 100% elongation (ASTM D412), elongation @ break % (ASTM D412), tensile strength (ASTM D412), and Die C Tear (ASTM D624). The results are shown in Table 1.

EXAMPLE 2

[0059] An elastomer composition was prepared according to the procedure of Example 1, except that 20 PHR of Natrorez 25, a natural resin coal tar derived plasticizer available from Harwick of Akron, Ohio, was added to the composition. The cured elastomer material was measured for Tg by DMTA, Shore A Hardness, 100% elongation, elongation @ break %, tensile strength, and Die C Tear. The results are shown in Table 1.

EXAMPLE 3

[0060] An elastomer composition was prepared according to the procedure of Example 1, except that 20 PHR of Paraplex G 25, a polysebacate plasticizer, available from C.P. Hall of Chicago, Illinois, was added to the composition. The cured elastomer material was measured for Tg by DMTA, Shore A Hardness, 100% elongation, elongation @ break %, tensile strength, and Die C Tear. The results are shown in Table 1.

EXAMPLE 4

[0061] An elastomer composition was prepared according to the procedure of Example 1, except that 20 PHR of lauryl methacrylate (LMA) monomer was added as a plasticizer to the composition, 7.5 PHR of DCP40 was used and the cured elastomer was heat aged at 100 deg C for 70 hours in a forced air oven. The cured/heat aged elastomer material was measured for Tg by DMTA, Shore A Hardness, 100% elongation, elongation @ break %, tensile strength, and Die C Tear. The results are shown in Table 1.

Table 1

Property	Example 1 (no plasticizer)	Example 2 (Natrorez 25)	Example 3 (Paraplex G 25)	Example 4 (LMA)
Tg by DMTA	-5.5 °C	-5.1 °C	-7.5 °C	-11.3 °C
Shore A Hardness	73	62	62	59

Table 1 (continued)

Property	Example 1 (no plasticizer)	Example 2 (Natrez 25)	Example 3 (Paraplex G 25)	Example 4 (LMA)
100% elongation	5.98 (867 psi)	2.12 (308 psi)	3.04 MPa (441 psi)	1.68 MPa (273 psi)
elongation @ break %	245	526	274	420
tensile strength	22.6 MPa (3285psi)	17.7 MPa (2567psi)	16.5 MPa (2397psi)	16.2 MPa (2349psi)
Die C Tear	254	264	193	218

[0062] The physical testing of the elastomer compositions of Examples 1-4 illustrates that the elastomer composition of the present invention (Example 4) is comparably or more efficiently plasticized. The Example 4 elastomer composition has a lower T_g and lower Shore A hardness than the elastomer composition with no plasticizer or those having conventional plasticizers (Examples 1-3). Furthermore, the lower PSI at 100% elongation and the % elongation at break also indicate more efficient plasticization of the elastomer composition of the present invention. Strength in tensile and Die C tear is similar to the elastomer compositions with conventional plasticizers.

EXAMPLES 5-8

[0063] Elastomer compositions were prepared as in Examples 1-4. The cured elastomer compositions were tested for solvent resistance by weight loss after immersion in chloroform at 40°C for 70 hours. The results are depicted in Table 2 as percent weight of extractables, percent weight plasticizer loss and for Example 4, percent plasticizer loss after heat aging. Examples 6 and 7 were not heat aged because of the unavailability of unsaturation on these molecules, during heat aging, which are needed to increase polymer molecular weight.

Table 2

Property	Example 5 (no plasticizer)	Example 6 (Natrez 25)	Example 7 (Paraplex G 25)	Example 8 (LMA)
%wt extractables	4.5	15.1	8.5	8.3
%wt plast. Loss	0	100	41	38
%wt loss after heat aging	-	-	-	13

[0064] The solvent resistance test using chloroform as a solvent shows the elastomer composition containing the poly-LMA polymerized in situ to be better than the Natrez 25 containing elastomer composition and slightly better than the Paraplex G 25 containing composition. However, when the composition is heat aged the resistance improves even more. The availability of unsaturation in the poly-LMA allows additional polymerization of the LMA which further lowers extraction of plasticizer from the elastomer composition.

EXAMPLE 9

Preparation of Fluoroelastomer Composition

[0065] An elastomer mixture containing:

	PHR
FLS 2650 (fluoroelastomer from 3M Co. - St. Paul, Minnesota)	100
Cri-D 82.5 (activator from Cri-Tech, Inc. - Hanover, Mass)	5
TAIC (cross-link accelerator from Mitsubishi Int'l Corp. New York, NY)	2
N 330 carbon Black (Cabot - Norcross, Georgia)	30

(continued)

	PHR
DC 60 (60% Dicumyl peroxide from Akrochem-Akron, Ohio)	2

was compounded by combining the materials in a Banbury mixer and mixing for 15 minutes while not heating up to a temperature of 100 deg C. No plasticizer was included in the elastomer composition. The green elastomer composition was cured at 160 deg C in a lab press. The cured elastomer material was measured for Tg by DMTA, Shore A Hardness, 100% elongation, elongation @ break %, tensile strength and was observed for molding compatibility. The results are shown in Table 4.

EXAMPLE 10

[0066] An elastomer composition was prepared according to the procedure of Example 9, except that 10 PHR of Paraplex G 40, a polysebacate plasticizer, available from C.P. Hall of Chicago, Illinois, was added to the composition. The cured elastomer material was measured for Tg by DMTA, Shore A Hardness, 100% elongation, elongation @ break %, tensile strength and was observed for molding compatibility. The results are shown in Table 4.

EXAMPLE 11

[0067] An elastomer composition was prepared according to the procedure of Example 1, except that 10phr of poly-LMA/SMA (95:5) copolymer was added to the composition and the elastomer composition was post-cured per recommendations of the manufacturer, 3M Co.

[0068] The poly-LMA/SMA (95:5) copolymer was prepared as follows. A 5 liter reaction vessel was fitted with a thermometer, a temperature controller, a purge gas inlet, a water-cooled reflux condenser with purge gas outlet, a stirrer, and an addition funnel. To the addition funnel was charged 3354.91 grams of a homogeneous monomer mixture of 168.39 grams cetyl-stearyl methacrylate (SMA, 96.5% purity), 3134.52 grams lauryl-myristyl methacrylate (LMA, 98.5% purity), 3.25 grams of Vazo-67, and 48.75 grams dodecyl mercaptan. Thirty percent (1006.47grams) of the monomer mixture in the addition funnel was charged to the reaction vessel which was then flushed with nitrogen for ~30 minutes before applying heat to bring the contents of the reaction vessel to 120°C. When the contents of the vessel reached 120°C, the balance of the monomer mixture in the addition funnel was uniformly charged to the reaction vessel over 60 minutes. At the end of the monomer mixture addition, the reaction vessel contents were maintained at 120°C for 30 minutes. At the end of the 30 minute hold, the polymerization temperature was reduced to 105°C before adding the first of two discrete chaser shots of initiator, each consisting of 6.50 grams of a Vazo-67. Thirty minutes after adding the first chaser initiator shot, the second chaser shot of initiator was added to the reaction while maintaining the temperature of the reaction vessel contents at 105°C. Thirty minutes after the second initiator chaser shot, the batch temperature was increased to 120°C and held at temperature for 30 minutes to ensure complete consumption of initiator. The product so formed exhibited a polymer solids content of 97.7 wt. % (by GPC assay), a viscosity of 9.2×10^{-5} m²/g at 98.8°C (920 cSt at 210°F) and a molecular weight (Mw) of 24,700.

[0069] The LMA/SMA product was tested for heat stability. The co-polymer was charged to a flask and heated in an inert atmosphere for about 24 hrs. at 232°C (450°F). The samples were run both with (0.5%) and without catalyst (dicumyl peroxide). The results follow in Table 3.

Table 3

Time	Catalyst?	Mw	Mn
Initial -0 hours	Yes	26,800	20,900
2 hours	Yes	27,600	21,200
6 hours	Yes	27,300	21,100
22 hours	Yes	27,400	21,100
Initial- 0 hours	No	26,800	20,900
4 hours	No	26,500	20,800
20 hours	No	26,200	20,600

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[0070] As illustrated in Table 3, stability at 232°C was excellent.

[0071] The elastomer product was measured for Tg by DMTA, Shore A Hardness, 100% elongation, elongation @ break %, tensile strength and was observed for molding compatibility. The results are shown in Table 4.

EXAMPLE 12

[0072] An elastomer composition was prepared according to the procedure of Example 1, except that 10phr of terminally unsaturated butyl acrylate oligomer (o-BA) was added as a plasticizer to the composition and the cured elastomer composition was post-cured per recommendations of the manufacturer, 3M Co.

[0073] The terminally unsaturated o-BA was prepared as follows. A 35% solution of butyl acrylate (BA) monomer in acetone containing di t-butyl peroxide (2% based on monomer) was fed at 5 ml min. through a high pressure/temperature reactor at 275 °C and 24.1 MPa (3500 psi). The resultant sample was stripped on a rotovap to remove residual BA monomer and acetone. A proton NMR spectrum of this product was consistent with the expected structure and combined with mass spectroscopy (MS) indicated 70% of the oligomer chains possess terminal unsaturation. An FTIR spectrum of this material showed a carbonyl stretch at 1730 - 1740 cm⁻¹. The product oligomer was a clear, colorless fluid having the following properties:

Res. BA = 200 ppm

Total solids = 99.3 %

Tg = -71 °C

Mw = 2100*

Mn = 930*

Mw/Mn = 2.3

Viscosity = 0.016 Pa-s (160 cps).

*The molecular weights were determined with gel permeation chromatography using an o-BA standard. The cured elastomer material was measured for Tg by DMTA, Shore A Hardness, 100% elongation, elongation @ break %, tensile strength and was observed for molding compatibility. The results are shown in Table 4.

Table 4

Property	Example 9 (no plasticizer)	Example 10 (Paraplex G 40)	Example 11 (pLMA/SMA)	Example 12 (o-BA)
Tg by DMTA	11 °C	-	12 °C	8 °C
Shore A Hardness	92	95	90	96
PSI @100% elongation	8.93 MPa (1296 psi)	6.32 MPa (918 psi)	5.36 MPa (778 psi)	5.58 MPa (810 psi)
% elongation @ break	190	250	300	177
tensile strength	13.8 MPa (2000psi)	9.13 MPa (1325psi)	7.80 MPa (1132psi)	12.6 MPa (1821psi)
molding compatibility	yes	no	yes	yes

[0074] The elastomer composition of the present invention (Examples 11 and 12) has comparable Tg and Shore A hardness with the elastomer composition with no plasticizer or conventional plasticizers (Examples 9 and 10). Furthermore, the lower PSI at 100% elongation and the % elongation at break also indicate efficient plasticization of the elastomer composition of the present invention and exhibit enhanced processability. Strength in tensile is similar to the elastomer compositions with conventional plasticizers. The molding compatibility, that is the ability of the plasticizer to remain in the elastomer composition without a change in position and/or migration (bloomed) to the surface during molding. The elastomer compositions of the present invention exhibited compatibility with the fluoroelastomer whereas the Paraplex containing elastomer composition failed.

EXAMPLES 13-16

[0075] The elastomer compositions were prepared as in Examples 9-12. The elastomer compositions were tested for solvent resistance by immersion in diesel fuel at 40°C for 100 hours. The resultant physicals were measured again

and are depicted in Table 5.

Table 5

Property	Example 13 (no plasticizer)	Example 14 (Paraplex 40)	Example 15 (pLMA/SMA)	Example 16 (o-BA)
MPa (PSI) @ 100% elong	8.30 (1205)	6.61 (959)	4.92 (714)	5.63 (817)
% elong @ break	179	173	288	216
Tensile MPa (PSI)	11.8 (1708)	10.0 (1454)	7.05 (1022)	8.22 (1193)

[0076] A comparison of the results exhibited in Table 4 (before extraction) and those in Table 5 (after extraction) illustrate the increased resistance to extraction in the elastomer compositions of the present invention and the loss of compatibility of Paraplex 40 during the molding /curing of the elastomer composition. The elastomer compositions of the present invention show comparable or increased plasticization after diesel extraction and the conventional elastomer composition shows a decrease in plasticization when Table 4 (before extraction) and Table 5 (after extraction) are compared.

Claims

1. An elastomer composition, comprising:

(A) at least one elastomer;

(B) a plasticizer comprising at least one polymeric material, having a weighted average molecular weight of (Mw) of 500 to 1,000,000, formed from at least one ethylenically unsaturated monomer selected from the group consisting of:

(i) at least one monomer selected from the group consisting of (meth)acrylic acid; C₁₀-C₅₀alkyl (meth)acrylates; and C₁-C₅₀alkyl (meth)acrylates substituted with halogen, nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino, alkylamino or dialkylamino; and

(ii) optionally, at least one monomer selected from the group consisting of vinylaromatic monomers, optionally substituted with one or more halogen, nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino, or alkylamino group; nitrogen-containing ring compounds and thio analogs thereof, optionally substituted with C₁-C₆alkyl; vinyl acetate; vinyl chloride; vinyl fluoride; vinyl bromide; vinylidene chloride; vinylidene fluoride; vinylidene bromide; (meth)acrylonitrile; (meth)acrylamide; and dialkylaminoC₂-C₆alkyl (meth)acrylamides, and

(C) a curing agent,

wherein the at least one polymeric material is substantially permanent within the elastomer, such that, during mixing in or with the elastomer, molding or during use of any piece prepared from the elastomer composition, or in response to an external stimulus, the loss of polymeric material from the elastomer is less than 10 percent by weight of the total weight of the at least one polymeric material.

2. An elastomer composition according to claim 1, wherein the at least one ethylenically unsaturated monomer is selected from C₁₀- to C₂₀ alkyl (meth)acrylates and C₁-C₂₀alkyl (meth)acrylates substituted with halogen, nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino, alkylamino or dialkylamino.

3. An elastomer composition according to claim 2, wherein the at least one ethylenically unsaturated monomer is lauryl methacrylate.

4. An elastomer composition according to claim 1, wherein the at least one ethylenically unsaturated monomer is selected from C₂₀- to C₅₀ alkyl (meth)acrylates and C₂₀-C₅₀alkyl (meth)acrylates substituted with halogen, nitro, cyano, haloalkyl, carbalkoxy, carboxy, amino, alkylamino or dialkylamino.

5. An elastomer composition according to any one of the preceding claims, wherein the at least one polymeric material comprises a copolymer of lauryl methacrylate and stearyl methacrylate.

6. An elastomer composition according to any one of the preceding claims, wherein the at least one polymeric material is a terminally unsaturated (meth)acrylate oligomer.

7. An elastomer composition according to any one of the preceding claims, wherein the at least one elastomer is a styrene-butadiene elastomer, chloroprene elastomer, butyl elastomer, polybutadiene elastomer, nitrile elastomer, polyethylene elastomer, ethylene-propylene elastomer, acrylic elastomer, silicone elastomer, fluoroelastomer, epichlorohydrin elastomer, polyalkenamer elastomer, polysulfide elastomer, urethane elastomer, mixtures thereof or blends thereof.

8. An elastomer composition according to any one of the preceding claims, further comprising a filler.

9. An elastomer composition according to claim 8, wherein the filler is selected from carbon black, carbon fiber, calcium carbonate, natural and synthetic silica, talc, mica, wollastonite, glass spheres and glass fiber.

10. An elastomer composition according to any one of the preceding claims, further comprising a crosslinking accelerator.

11. A process for preparing an elastomer composition according to any one of the preceding claims, the process comprising:

(A) providing a mixture of an elastomer, at least one ethylenically unsaturated monomer selected from the group consisting of:

(i) at least one monomer selected from the group consisting of (meth)acrylic acid; C₁₀-C₅₀alkyl (meth)acrylates; and C₁-C₅₀alkyl (meth)acrylates substituted with halogen, nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino, alkylamino or dialkylamino; and

(ii) optionally, at least one monomer selected from the group consisting of vinylaromatic monomers, optionally substituted with one or more halogen, nitro, cyano, alkoxy, haloalkyl, carbalkoxy, carboxy, amino, or alkylamino group; nitrogen-containing ring compounds and thio analogs thereof, optionally substituted with C₁-C₆alkyl; vinyl acetate; vinyl chloride; vinyl fluoride; vinyl bromide; vinylidene chloride; vinylidene fluoride; vinylidene bromide; (meth)acrylonitrile; (meth)acrylamide; and dialkylaminoC₂-C₆alkyl (meth)acrylamides or a polymeric material having a weighted average molecular weight (Mw) of 500 to 1,000,000, formed from at least one ethylenically unsaturated monomer as hereinbefore defined, and a curing agent; and

(B) curing the elastomer composition, wherein during curing the at least one ethylenically unsaturated monomer, if present, is polymerized in situ to form an elastomer composition wherein the at least one polymeric material is substantially permanent within the elastomer, such that, during mixing in or with the elastomer, molding or during use of any piece prepared from the elastomer composition, or in response to an external stimulus, the loss of polymeric material from the elastomer is less than 10 percent by weight of the total weight of the at least one polymeric material.

12. The process of claim 11, further comprising:

(C) heat aging or post curing the cured elastomer composition.

13. A method of plasticizing an elastomer, comprising:

(A) providing an elastomer composition according to any one of claims 1 to 10, wherein the at least one polymeric material is present in an amount effective to plasticize the elastomer.

14. The method of claim 13, wherein the polymeric material is present from 2 to 100 PHR.

15. A method of enhancing processability of an elastomer, comprising:

(A) providing an elastomer composition according to any one of claims 1 to 10, wherein the at least one polymeric material is present in an amount effective to enhance processability of the elastomer.

16. The method of claim 15, wherein the polymeric material is present from 2 to 30 PHR.

Patentansprüche

1. Eine Elastomerzusammensetzung, umfassend:

(A) mindestens ein Elastomer;

(B) einen Weichmacher, umfassend mindestens ein polymeres Material mit einem durchschnittlichen Molekulargewicht (MG) von 500 bis 1.000.000, gebildet aus mindestens einem ethylenisch ungesättigten Monomer, ausgewählt aus der Gruppe, bestehend aus:

- (i) mindestens einem Monomer ausgewählt aus der Gruppe, bestehend aus (Meth)Acrylsäure: C₁₀-C₅₀-Alkyl(meth)acrylaten; und C₁-C₅₀-Alkyl(meth)acrylaten, substituiert mit Halogen, Nitro, Cyano, Alkoxy, Haloalkyl, Carbalkoxy, Carboxy, Amino, Alkylamino oder Dialkylamino; und
- (ii) optional mindestens einem Monomer ausgewählt aus der Gruppe, bestehend aus Vinylaromatmonomeren, optional substituiert mit einem oder mehreren Substituenten von Halogen, Nitro, Cyano, Alkoxy, Haloalkyl, Carbalkoxy, Carboxy, Amino oder Alkylamino; Stickstoff-enhaltenden Ringverbindungen und Thioanaloge davon, optional substituiert mit C₁-C₈-Alkyl; Vinylacetat; Vinylchlorid; Vinylfluorid; Vinylbromid; Vinylidenchlorid; Vinylidenfluorid; Vinylidenbromid; (Meth)acrylonitril; (Meth)acrylamid; und Dialkylamino-C₂-C₆-Alkyl(meth)acrylamiden, und

(C) ein Vernetzungsmittel,

wobei das mindestens eine polymere Material im Wesentlichen permanent innerhalb des Elastomers vorliegt, so dass während des Mischens in oder mit dem Elastomer, während des Formens oder während der Verwendung eines aus der Elastomerzusammensetzung hergestellten Stückes oder in Reaktion auf einen äußeren Stimulus der Verlust an polymerem Material aus dem Elastomer weniger als 10 Gewichtsprozent des Gesamtgewichts des mindestens einen polymeren Materials beträgt.

2. Eine Elastomerzusammensetzung gemäß Anspruch 1, wobei das mindestens eine ethylenisch ungesättigte Monomer ausgewählt ist aus C₁₀ - C₂₀-Alkyl(meth)acrylaten und C₁ - C₂₀-Alkyl(meth)acrylaten, substituiert mit Halogen, Nitro, Cyano, Alkoxy, Haloalkyl, Carbalkoxy, Carboxy, Amino, Alkylamino oder Dialkylamino.

3. Eine Elastomerzusammensetzung gemäß Anspruch 2, wobei das mindestens eine ethylenisch ungesättigte Monomer Laurylmethacrylat ist.

4. Eine Elastomerzusammensetzung gemäß Anspruch 1, worin das mindestens eine ethylenisch ungesättigte Monomer ausgewählt ist aus C₂₀-C₅₀-Alkyl(meth)acrylaten und C₂₀-C₅₀-Alkyl(meth)acrylaten, substituiert mit Halogen, Nitro, Cyano, Haloalkyl, Carbalkoxy, Carboxy, Amino, Alkylamino oder Dialkylamino.

5. Eine Elastomerzusammensetzung gemäß einem der vorangehenden Ansprüche, wobei das mindestens eine polymere Material ein Copolymer von Laurylmethacrylat und Stearylmethacrylat umfasst.

6. Eine Elastomerzusammensetzung gemäß einem der vorangehenden Ansprüche, wobei das mindestens eine polymere Material ein terminal ungesättigtes (Meth)acrylatoligomer ist.

7. Eine Elastomerzusammensetzung gemäß einem der vorangehenden Ansprüche, wobei das mindestens eine Elastomer ein Styrol-Butadienelastomer, Chloroprenelastomer, Butylelastomer, Polybutadienelastomer, Nitrilelastomer, Polyethylenelastomer, Ethylen-Propylenelastomer, Acryelastomer, Silikonelastomer, Fluorelastomer, Epichlorohydrinelastomer, Polyalkenamerelastomer, Polysulfididelastomer, Urethanelastomer, ein Gemisch oder eine Mischung davon ist.

8. Eine Elastomerzusammensetzung gemäß einem der vorangehenden Ansprüche, weiter umfassend einen Füllstoff.

9. Eine Elastomerzusammensetzung gemäß Anspruch 8, worin der Füllstoff ausgewählt ist aus Carbon Black, Kohlenstofffasern, Calciumcarbonat, natürlichem und synthetischem Siliciumoxid, Talkum, Mika, Wollastonit, Glasku-

geln und Glasfasern.

10. Eine Elastomerzusammensetzung gemäß einem der vorangehenden Ansprüche, weiter umfassend einen Vernetzungsbeschleuniger.

11. Ein Verfahren zur Herstellung einer Elastomerzusammensetzung gemäß einem der vorangehenden Ansprüche, das Verfahren umfassend:

(A) Bereitstellen eines Gemisches von einem Elastomer, mindestens einem ethylenisch ungesättigten Monomer, ausgewählt aus der Gruppe bestehend aus:

(i) mindestens einem Monomer, ausgewählt aus der Gruppe, bestehend aus (Meth)Acrylsäure; C₁₀-C₅₀-Alkyl(meth)acrylaten; und C₁-C₅₀-Alkyl(meth)acrylaten, substituiert mit Halogen, Nitro, Cyano, Alkoxy, Haloalkyl, Carbalkoxy, Carboxy, Amino, Alkylamino oder Dialkylamino; und

(ii) optional mindestens einem Monomer, ausgewählt aus der Gruppe, bestehend aus Vinylaromatmonomeren, optional substituiert mit einem oder mehreren Substituenten von Halogen, Nitro, Cyano, Alkoxy, Haloalkyl, Carbalkoxy, Carboxy, Amino oder Alkylamino; Stickstoff-enthaltenden Ringverbindungen und Thioanaloga davon, optional substituiert mit C₁-C₈-Alkyl; Vinylacetat; Vinylchlorid; Vinylfluorid; Vinylbromid; Vinylidenchlorid; Vinylidenfluorid; Vinylidenbromid; (Meth)acrylonitril; (Meth)acrylamid; und Dialkylamino-C₂-C₆-Alkyl(meth)acrylamiden oder ein polymeres Material mit einem durchschnittlichen Molekulargewicht (MG) von 500 bis 1.000.000, gebildet aus mindestens einem ethylenisch ungesättigten Monomer, wie vorangehend definiert, und einem Vernetzungsmittel; und

(B) Vernetzen der Elastomerzusammensetzung, wobei während des Vernetzens das mindestens eine ethylenisch ungesättigte Monomer, soweit anwesend, in situ polymerisiert wird, um eine Elastomerzusammensetzung zu bilden, in der das mindestens eine polymere Material im Wesentlichen permanent innerhalb des Elastomers ist, so dass während des Mischens in oder mit dem Elastomer, während des Formens oder während der Verwendung eines aus der Elastomerzusammensetzung hergestellten Stückes oder in Reaktion auf einen äußeren Stimulus der Verlust an polymerem Material aus dem Elastomer weniger als 10 Gewichtsprozent des Gesamtgewichts des mindestens einen polymeren Materials beträgt.

12. Das Verfahren nach Anspruch 11, weiter umfassend:

(C) Hitzealterung oder Nachhärtung der vernetzten Elastomerzusammensetzung.

13. Ein Verfahren zum Weichmachen eines Elastomers, umfassend:

(A) Bereitstellung einer Elastomerzusammensetzung gemäß einem der Ansprüche 1 bis 10, wobei das mindestens eine polymere Material in einer Menge anwesend ist, die das Elastomer wirksam plastifiziert.

14. Das Verfahren nach Anspruch 13, wobei das polymere Material anwesend ist von 2 bis 100 PHR.

15. Ein Verfahren zur Verbesserung der Verarbeitbarkeit eines Elastomers, umfassend:

(A) Bereitstellung einer Elastomerzusammensetzung gemäß einem der Ansprüche 1 bis 10, worin das mindestens eine polymere Material in einer Menge anwesend ist, die die Verarbeitbarkeit des Elastomers wirksam erhöht.

16. Das Verfahren nach Anspruch 15, worin das polymere Material anwesend ist von 2 bis 30 PHR.

Revendications

1. Composition élastomère, comprenant

(A) au moins un élastomère ;

(B) un plastifiant comprenant au moins un matériau polymère, ayant une masse moléculaire moyenne en masse (Mw) de 500 à 1 000 000, formé à partir d'au moins un monomère à insaturation éthylénique choisi

dans l'ensemble comprenant :

- (i) au moins un monomère choisi dans l'ensemble comprenant l'acide (méth)acrylique ; les (méth)acrylates d'alkyle en C_{10} - C_{50} ; et les (méth)acrylates d'alkyle en C_1 - C_{50} substitués par des substituants halogéno, nitro, cyano, alcoxy, halogénoalkyle, carbalcoxy, carboxy, amino, alkylamino ou dialkylamino ; et
- (ii) éventuellement, au moins un monomère choisi dans l'ensemble comprenant les monomères vinyloaromatiques, éventuellement substitués par un ou plusieurs groupes halogéno, nitro, cyano, alcoxy, halogénoalkyle, carbalcoxy, carboxy, amino ou alkylamino ; les composés cycliques azotés et leurs analogues thio, éventuellement substitués par des substituants alkyle en C_1 - C_8 ; l'acétate de vinyle ; le chlorure de vinyle ; le fluorure de vinyle ; le bromure de vinyle ; le chlorure de vinylidène ; le fluorure de vinylidène ; le bromure de vinylidène ; le (méth)acrylonitrile ; le (méth)acrylamide et les dialkylamino(alkyle en C_2 - C_6) (méth)acrylamides, et

(C) un agent durcisseur,

où au moins un matériau polymère est d'une manière pour ainsi dire permanente situé à l'intérieur de l'élastomère de telle sorte que, pendant le mélange dans l'élastomère ou à l'élastomère, le moulage, ou encore l'utilisation d'une pièce quelconque préparée à partir de la composition élastomère, ou en réponse à un stimulus externe, la perte de matériau polymère à partir de l'élastomère soit inférieure à 10 % en poids par rapport au poids total du ou des matériaux polymères.

2. Composition élastomère selon la revendication 1, dans laquelle l'au moins un monomère à insaturation éthylénique est choisi parmi les (méth)acrylates d'alkyle en C_{10} - C_{20} , et les (méth)acrylates d'alkyle en C_1 - C_{20} substitués par des substituants halogéno, nitro, cyano, alcoxy, halogénoalkyle, carbalcoxy, carboxy, amino, alkylamino ou dialkylamino.
3. Composition élastomère selon la revendication 2, dans laquelle l'au moins un monomère à insaturation éthylénique est le méthacrylate de lauryle.
4. Composition élastomère selon la revendication 1, dans laquelle l'au moins un monomère à insaturation éthylénique est choisi parmi les (méth)acrylates d'alkyle en C_{20} - C_{50} et les (méth)acrylates d'alkyle en C_{20} - C_{50} substitués par des substituants halogéno, nitro, cyano, halogénoalkyle, carbalcoxy, carboxy, amino, alkylamino ou dialkylamino.
5. Composition élastomère selon l'une quelconque des revendications précédentes, dans laquelle l'au moins un matériau polymère comprend un copolymère de méthacrylate de lauryle et de méthacrylate de stéaryle.
6. Composition élastomère selon l'une quelconque des revendications précédentes, dans laquelle l'au moins un matériau polymère est un oligomère de (méth)acrylate à insaturation terminale.
7. Composition élastomère selon l'une quelconque des revendications précédentes, dans laquelle l'au moins un élastomère est un élastomère styrène-butadiène, un élastomère chloroprène, un élastomère butyl, un élastomère polybutadiène, un élastomère nitrile, un élastomère polyéthylène, un élastomère éthylène-propylène, un élastomère acrylique, un élastomère silicone, un fluoroélastomère, un élastomère épichlorhydrine, un élastomère polyalcénamère, un élastomère polysulfure, un élastomère uréthane, leurs mélanges ou mélanges homogènes.
8. Composition élastomère selon l'une quelconque des revendications précédentes, qui comprend en outre une charge.
9. Composition élastomère selon la revendication 8, dans laquelle la charge est choisie parmi le noir de carbone, les fibres de carbone, le carbonate de calcium, la silice naturelle et la silice synthétique, le talc, le mica, la wollastonite, les sphères de verre et les fibres de verre.
10. Composition élastomère selon l'une quelconque des revendications précédentes, qui comprend en outre un accélérateur de réticulation.
11. Procédé de préparation d'une composition élastomère selon l'une quelconque des revendications précédentes, le procédé comprenant :

(A) la mise à disposition d'un mélange d'un élastomère, d'au moins un monomère à insaturation éthylénique choisi dans l'ensemble comprenant :

(i) au moins un monomère choisi dans l'ensemble comprenant l'acide (méth)acrylique ; les (méth)acrylates d'alkyle en C_{10} - C_{50} ; et les (méth)acrylates d'alkyle en C_1 - C_{50} substitués par des substituants halogéno, nitro, cyano, alcoxy, halogénoalkyle, carbalcoxy, carboxy, amino, alkylamino ou dialkylamino ; et
 (ii) éventuellement, au moins un monomère choisi dans l'ensemble comprenant les monomères vinyla-
 romatiques, éventuellement substitués par un ou plusieurs groupes halogéno, nitro, cyano, alcoxy, halogé-
 noalkyle, carbalcoxy, carboxy, amino ou alkylamino ; les composés cycliques azotés et leurs analogues
 thio, éventuellement substitués par des substituants alkyle en C_1 - C_8 ; l'acétate de vinyle ; le chlorure de
 vinyle ; le fluorure de vinyle ; le bromure de vinyle ; le bromure de vinylidène ; le fluorure de vinylidène ;
 le bromure de vinylidène ; le (méth)acrylonitrile ; le (méth)acrylamide et les dialkylamino(alkyle en C_2 - C_6)
 (méth)acrylamides ou un matériau polymère ayant une masse moléculaire moyenne en masse (Mw) de
 500 à 1 000 000, formé à partir d'au moins un monomère à insaturation éthylénique tel que défini ci-
 dessus, et un agent durcisseur ; et

(B) le durcissement de la composition élastomère, où, pendant le durcissement, l'éventuel au moins un mo-
 nomère à insaturation éthylénique est polymérisé in situ pour former une composition élastomère dans laquelle
 l'au moins un matériau polymère est pour ainsi dire présent d'une manière permanente à l'intérieur de l'élas-
 tomère, de telle sorte que, pendant le mélange dans l'élastomère ou à l'élastomère, le moulage, ou encore
 l'utilisation d'une pièce quelconque préparée à partir de la composition élastomère, ou en réponse à un sti-
 mulus externe, la perte de matériau polymère à partir de l'élastomère soit inférieure à 10 % en poids par
 rapport au poids total du ou des matériaux polymères.

12. Procédé selon la revendication 11, qui comprend en outre :

(C) le vieillissement thermique ou le post-durcissement de la composition élastomère durcie.

13. Procédé de plastification d'un élastomère, qui comprend :

(A) la mise à disposition d'une composition élastomère selon l'une quelconque des revendications 1 à 10, l'au
 moins un matériau polymère étant présent en une quantité efficace pour plastifier l'élastomère.

14. Procédé selon la revendication 13, dans lequel le matériau polymère est présent en une quantité de 2 à 100 PHR
 (parties pour 100 parties de résine).

15. Procédé pour améliorer l'aptitude à la mise en oeuvre d'un élastomère, qui comprend :

(A) la mise à disposition d'une composition élastomère selon l'une quelconque des revendications 1 à 10, l'au
 moins un matériau polymère étant présent en une quantité efficace pour améliorer l'aptitude de l'élastomère
 à la mise en oeuvre.

16. Procédé selon la revendication 15, dans lequel le matériau polymère est présent en une quantité de 2 à 30 PHR.